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FOOD CHAIN BIOMAGNIFICATION OF HEAVY METALS IN SAMPLES FROM THE LOWER PRUT FLOODPLAIN NATURAL PARK

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Abstract

Pollutants transfer via the food chain was investigated in a wetland ecosystem from the Lower Prut Floodplain Natural Park in Romania. Trace elements (Cd, Cu, Pb and Zn) were determined by Inductively Coupled Plasma – Optical Emission Spectrometry (ICP-OES) from samples belonging to primary producers and primary and secondary consumers, and also from water and sediments samples. Non-essential trace elements as Cd and Pb exhibited low concentrations in molluscs and fish, but zinc had shown concentration up to 745.28 μg/g in *Cyprinus carpio*.

Key words: bioaccumulation, food chains, heavy metals, Prut River

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1. Introduction

Xenobiotics bioaccumulation by living organisms depending on their position in the food pyramid is a widely debated aspect (Ruelas-Inzunza and Paez-Osuna, 2008), being one of the most severe threats to species perpetuation, together with habitats degradation, diseases, climate changes, introduction of predators or competitive species (Primack et al., 2008). The presence of compounds like heavy metals or persistent organic pollutants might generate catastrophic effects on the ecosystems they are released in, including the extinction of certain species living in those areas (Ratcliffe, 1967).

Due to the unique characteristics they posses, wetlands are of a great importance for the environment, being the ecotone between the terrestrial and aquatic ecosystems (Barker and Maltby, 2009). Due to the fluctuant level of water, intense biogeochemical processes are taking place, determining frequent changes in nutrients balance and subsequently ecosystem evolution (Verhoeven, 2009). Lower Prut Floodplain Natural Park is a recently established protected area along the South-Eastern border of Romania with Moldova, including the wetlands and lakes from the inferior sector of the Prut River. Covering a surface of more than 8000 ha, the park hosts significant resources of wildlife, together with habitats of a communitarian importance, two European Natura 2000 sites overlapping the park area (Natura 2000 code ROSCI0105 and ROSCI0213). Prior to entering the Lower Prut Floodplain Natural Park, the Prut River passes more than 900 km, collecting the water from a 27,000 km^2 watershed, the pollution sources being agricultural and industrial (Balteanu et al., 2006).

Whereas for mercury it is clearly stated that it has the capacity to biomagnify along the food chains

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(Dietz et al., 2000), for other metals and metalloids the conclusions of different studies are contradictory. Croteau et al. (2005) suggest that Cd accumulates into the freshwater aquatic organisms (macrophytes, fish), but they are not transferred in the next levels of the food chain Wren et al. (1995). Jara-Marini et al. (2009) identify a partial positive transference of Cu and Zn from the phytoplankton to crab; Ikemoto et al. (2008) observe no dependence between the trophic level and concentration of Cu, Zn, Pb Cd and 13 other trace elements in the Mekong Delta.

The aim of this study was (a) to quantify the concentration of some heavy metals (Cd, Cu, Pb, Zn) in different levels of the Lower Prut wetland food chains, and (b) to assess the extent of these elements transfer from primary producers to primary and secondary consumers.

2. Experimental

The water and sediments samples were collected from 6 transects along the considered river sector based on a prospective sampling plan, considering the existing human activities in the area that might produce changes in water quality. The six locations are located as it follows: 1 – near the Maţa – Rădeanu fish ponds, where the Prut River enters Galati County (northern limit of the Lower Prut Floodplain Natural Park); 2 – downstream of Pochina and Leahu lakes and village of Rogojeni; 3 – downstream of Vlădeşti, Şovârca and Măicaş lakes and localities like Oancea, Slobozia-Oancea and Vlădeşti; 4 – downstream of Vlăşcuţa lake (Romanian side) and Manta lake (Republic of Moldova) and Brăneşti and Măstăcani villages; 5 – near the village of Şiviţa, influenced by the Beleu lake (Moldova); 6 – upstream of Prut River – Danube River junction, influences from Brateş lake and agricultural fields in the area, closest to the city of Galaţi.

Four campaigns have been performed for the water samples, in May 2009, July 2009, September 2010, and November 2010. The water samples were collected in high density polyethylene bottles and HNO_3 (Merck, 65%) was added immediately in order to prevent analyte losses. Sediments were collected in September 2010 from the first 5 cm of the alluvial sediments bed. Samples were stored in teflon boxes and frozen prior to chemical analysis.

Plant species samples were collected directly from the water surfaces in the water sampling locations and stored in plastic bags. Molluscs were collected from the submerged vegetation they were attached to (*Viviparus sp.*) or from the riverbed sediments (*Sinanodonta woodiana*) and their soft body was considered for analysis. Fish was purchased directly from the local fishermen and liver and muscle samples were collected from each individual.

Biological samples (plants, molluscs and fish) were frozen at -20 ^oC immediately after collection prior to acid digestion. Biological samples digestion was performed with concentrated acids (HNO_3:$HClO_4$ 2:1), until the complete destruction of the organic matrix. Sediments digestion has been made in an open system with concentrated acids (HF, HCl, $HClO_4$, HNO_3) followed by alkaline melting as described in Matache et al. (2002). If not indicated otherwise, all reagents used (acids) were of analytical grade and were purchased from Sigma-Aldrich.

Heavy metals determination was made using Inductively Coupled Plasma – Optical Emission Spectrometry (ICP-OES). The method and its parameters have been described in detail in Matache et al. (2009). The detection limits for the method were 0.1 ppb (Cd, Cu), 1.5 ppb (Pb) and 0.5 ppb (Zn).

3. Results and discussion

The concentrations of the four trace elements considered in the survey in water and sediments samples are displayed in Table 1. For the water samples, the concentrations are presented as an average of each element concentration in the four campaigns of water samples collection. The results for Cd are not available as its concentration exceeded the detection limit only in one of the four months so it is either a case of momentary contamination (probably a release from sediments due to the flooding or (less likely) analytical method issue. For sampling site no. 4, all the samples collected for Pb were below the detection limit.

Trace elements concentration in water samples is quite heterogeneous (see the high values of the standard deviations), as a consequence of oscillating water level, as flooding affecting the river and adjacent lakes several times between May 2009 and November 2010. The concentration of copper (in 2 situations) and lead (in one situation) exceed the maximum admitted concentration in freshwater bodies (1st category of water quality according to the Romanian regulations, Ministry of Environment and Water Management, 2006).

Metals concentration in sediments trend is to increase along the analysed sector (from sampling point 1 to sampling point 6). An explanation would be that sampling point no. 6 is the closest one to Galati, the largest city in the region and the host of Arcelor Mittal steel plant (the largest in Romania), emphasizing distance pollution with metals. Another explanation might be that the sampling point is located in the close vicinity of the Prut River – Danube River junction. Differences in water chemistry of two bodies that get in contact (mainly differences of common ions concentration – Ca, Mg, HCO_3^-) can determine salts precipitation and trace elements coprecipitate with, being included in the riverbed sediments (situation described for Danube River – Cerna River junction in Matache et al., 2002).

Issues related to MAC exceeding appear also for copper (see Table 1). Trace elements concentration in the fish samples has been calculated in two steps as it follows: i) the median of the elements concentration in the liver and muscle of each individual and ii) the average and standard deviation of each species representatives medians.

Table 1. Trace elements concentration in Prut river water and sediment samples (concentration in µg/L for water samples and µg/g for sediment samples)

Section	*Cu*	*MAC**	*Cd*	*MAC*	*Pb*	*MAC*	*Zn*	*MAC*
Water								
1	7.88±5.97	20	NA*	0.50	1.25±1.50	5	10.40±1.70	100
2	24.96±28.71	20	NA	0.50	2.47±2.69	5	10.20±3.11	100
3	26.03±27.01	20	NA	0.50	6.16±10.52	5	9.00±1.41	100
4	16.85±19.72	20	NA	0.50	NA*	5	16.00±12.16	100
5	10.78±4.85	20	NA	0.50	0.83±1.65	5	8.55±1.34	100
6	12.04±12.27	20	NA	0.50	3.23±5.26	5	6.70±2.55	100
Sediments								
1	31.90	40	0.26	0.80	6.25	85	40.20	150
2	67.00	40	0.36	0.80	8.85	85	60.50	150
3	33.40	40	0.33	0.80	8.44	85	48.00	150
4	34.82	40	0.43	0.80	10.90	85	63.3	150
5	38.20	40	0.43	0.80	10.70	85	63.3	150
6	46.70	40	0.53	0.80	15.30	85	78.6	150

**MAC – Maximum admitted concentration – for water samples, 1st category of quality; *NA – not available; in yellow: situations where the concentration exceeds the MAC*

Table 2. Trace elements concentration in biological samples: primary producers, primary and secondary consumers (in µg/g) as average concentration ± standard deviation

Species	*Cu*	*Cd*	*Pb*	*Zn*
Primary producers				
A1. Salvinia natans (n=6)	20.59±4.39	0.31±0.11	4.80±2.39	41.37±4.98
A2. Elodeea canadensis (n=2)	18.97±1.75	0.86±0.06	4.83±1.03	79.20±56.74
Primary consumers				
B1. Viviparus sp. (n=7)	3.31±3.77	0.01±0.03	0.02±0.05	**ND***
B2. Sinanodonta woodiana (n=4)	0.49±0.26	0.01±0.02	0.00±0.00	**ND**
Secondary consumers				
C1. Cyprinus carpio (n=4)	7.03±8.04	0.10±0.07	0.00±0.00	323.51±269.89
C2. Carassius gibelio (n=3)	1.05±0.23	0.02±0.01	0.01±0.02	77.27±8.75

*n – Number of species representatives; *ND – not determined*

The use of medians instead of average values has been decided as the concentration of some elements such as Cd and Pb are usually higher in liver than in muscle (Marcussen et al., 2007). Zinc and copper are essential elements that appear in the environment components and living organisms as part of their metabolic and physiological processes (Garrett, 2000), but when exceeding certain levels, they become toxic for the species accumulating them (O'Shea and Geraci, 1999).

For *Cyprinus carpio*, zinc concentration varied from 14.10 µg/g and 745.28 µg/g, similar to the results of Bevoets et al. (2009), where the metal presence is attributed mainly to food chain accumulation than to water pollution. Zn also exhibits significant levels in *Carassius gibelio*, between 68.24 and 85.71 µg/g. Concentration levels for elements with an increased toxicity such as Cd and Pb are much lower in the analysed samples. Cadmium concentration in *Cyprinus carpio* exceeds the threshold value of the European Commission regulation for fish samples - 0.05 ppm – (European Commission, 2002), while the lead concentration in the same species fulfills the above-mentioned requirement (0.20 ppm).

The low levels of concentration require a larger number of samples in order to reduce possible errors in chemical analysis. No issues are generated by any of the toxic elements (Cd, Pb) for *Carassius gibelio*.

In what regards metals transfer along the food chain, the biomagnification factors, calculated as the ratio between metal concentration in the predator body and in the prey (Ciesielski et al., 2006), the results obtained for the six considered species are shown in Table 3. Unfortunately, the lack of results for Zn in primary consumers prevents us from drawing any conclusions on its food chain transfer. Lead is accumulated by the primary producers, but it is either not subsequently transferred to consumers or the molluscs eliminate it through metabolic processes (e.g. excretion).

Values of the biomagnification factor higher than 1 are recorded for copper transfer from primary consumers (*Viviparus sp.* and *Sinanodonta woodiana*) to *Cyprinus carpio* (2.12 and 14.35 respectively), but the trend is not respected between levels 1 and 2 of the trophic chain, the metal concentration being much higher in the plant species than in the molluscs soft body.

Table 3. Biomagnification factors for every two consecutive trophic levels
(A1, A2, B1, B2, C1, C2 – species coordinates as indicated in Table 1)

Cu	A1	0.16	B1	2.12	C1	**Cd**	A1	0.03	B1	10	C1
	A1	0.16	B1	0.32	C2		A1	0.03	B1	2	C2
	A1	0.02	B2	14.35	C1		A1	0.03	B2	10	C1
	A1	0.02	B2	2.14	C2		A1	0.03	B2	2	C2
	A2	0.17	B1	2.12	C1		A2	0.01	B1	10	C1
	A2	0.17	B1	0.32	C2		A2	0.01	B1	2	C2
	A2	0.03	B2	14.35	C1		A2	0.01	B2	10	C1
	A2	0.03	B2	2.14	C2		A2	0.01	B2	2	C2
Pb	A1	0	B1	0	C1	**Zn**	A1	-	B1	-	C1
	A1	0	B1	0.5	C2		A1	-	B1	-	C2
	A1	0	B2	NA	C1		A1	-	B2	-	C1
	A1	0	B2	NA	C2		A1	-	B2	-	C2
	A2	0	B1	0	C1		A2	-	B1	-	C1
	A2	0	B1	0.5	C2		A2	-	B1	-	C2
	A2	0	B2	NA	C1		A2	-	B2	-	C1
	A2	0	B2	NA	C2		A2	-	B2	-	C2

**NA – Not available*

Situation is similar for cadmium, with biomagnification factors values of 2 and 10 from primary to secondary consumers, but with practically no transfer from plants to molluscs. For cadmium, the reduced concentration level increases the data uncertainty. In both cases, the metals concentration in water might have a greater contribution than biomagnification through food.

4. Conclusions

Zinc and copper are the dominant trace elements of the Prut River wetland ecosystems, exhibiting significant concentrations in both environmental and biological samples. The zinc concentration in fish samples (an important resource for the local community) requires an extended analysis in order to evaluate the ecotoxicological risk involved. Only traces of the elements with a high toxicity (Cd, Pb) appear in the molluscs and fish samples. Partial bioaccumulation appears for copper and cadmium, but not along entire food chains, but for sequences of it. Elements concentration dynamics is influenced by frequent changes in water level and regime (from severe drought, when the adjacent lakes completely lose their water to long-term flooding and sediments dispersion into the water column).

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